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Aging Behavior of Reactive Air Brazed Seals for SOFC

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Abstract

The mechanical integrity of solid oxide fuel cells (SOFC) and the long-term stability under operating conditions are basic requirements for a reliable operation of SOFC stacks. In this respect the use of metallic brazes as sealing material is considered to have advantages in comparison to the widely used brittle glasses or glass ceramics. In this study the mechanical properties of reactive air brazed YSZ-steel joints and their long-term stability at high temperatures in air and dual atmospheres are investigated. Silver-based braze compositions like Ag-4CuO are used for reactive air brazing of gas tightness samples. During aging in air at 850°C for 800 h the thickness of the interfacial oxide layers increases with time, while the bending strength decreases. Microstructural analysis reveals the formation of voids within the brazing zone and the development of multilayered reaction layers. In contrast, the aging in dual atmospheres at 850°C causes strong degradation and the total loss of gas tightness. However, the addition of small amounts of TiH₂ to the braze compositions enhances the dual atmosphere tolerance of the reactive air brazed seals.

Introduction

Solid oxide fuel cells (SOFC) are becoming of increasing interest as power conversion units for fossil and biomass fuels in today's industrial market due to a number of advantages including: high efficiency, low emissions and potential use in a wide range of applications. In general, SOFCs consist of ceramic cell and different metallic components which have to be joined and sealed gas tight for operation at high temperatures up to 850°C in reducing and oxidizing atmospheres. Appropriate sealing materials have to match the thermal expansion coefficients of stack components, must withstand the harsh chemical environment and have to show good long-term stability under operating conditions. Especially in electrolyte supported SOFC the joints between the thin ceramic electrolytes made of zirconia and the metallic interconnector plates are critical.

The state-of-the-art joining technology for SOFC stacks are full or even partial crystalline glass ceramics that can be tailored in their softening, crystallization and thermal expansion behavior to correspond with the operating conditions and applied materials of different SOFC types [1-2]. However, despite their widespread application glasses and glass ceramics are afflicted with several drawbacks like cracks and bubbles in the glass seals or extensive foaming of the glasses at high temperatures [3]. Additionally, degradation processes are observed at the interfaces between the sealing glasses, the materials joined, and the surrounding atmospheres [4-6]. A promising alternative for sealing SOFC are metal based brazes which can be utilized by active metal brazing or reactive air brazing (RAB) processes. However, the active metal brazing process requires an oxygen-free environment like protective atmospheres (i.e. argon) or vacuum ($p < 10^{-4}$ mbar) which makes it necessary that all SOFC materials have to be stable at low oxygen partial pressure. Unfortunately, interesting cathode materials like perovskites cannot survive the active metal brazing process [7]. Therefore the joining activities for SOFC focus on reactive air brazing.

1. Scientific Approach

The RAB process is carried out in air with an oxidation stable braze filler metal. So far, exclusively silver based braze filler metals with varying contents of copper oxide and sometimes small additions of titanium oxide or others have been investigated for joining SOFC materials [8]. Most of the studies focus on enhancement of wetting behavior and development of new braze compositions [9-11]. Additionally, some papers publish results on mechanical properties of reactive air brazed joints mainly gained at room temperature of non-aged samples [12-14]. However, about the high temperature behavior and especially the long-term stability of reactive air brazed SOFC seals only less information is available [15-17]. In order to estimate the lifetime and reliability of reactive air brazed SOFC joints at higher temperatures, we have investigated the gas tightness and microstructure of reactive air brazed seals at 850°C for up to 800 h.

2. Experimental

For planar SOFC stacks with electrolyte supported cells (ESC), special ferritic (Fe-Cr) alloys are used as interconnect materials due to its low thermal coefficient of expansion close to the ceramic electrolyte, good oxidation resistance and low contact resistances at high temperatures. In this study, the ferritic stainless steel Crofer[®] 22 APU (ThyssenKrupp VDM, here always written as Crofer) was used. For sample preparation blank metal sheets were laser cut and the surface of the metallic joining partners was gently grind with SiC

paper to smooth the cutting edges and remove splashes. As ceramic joining partner zirconia stabilized with 3 mol-% yttria (3YSZ) was used, as this is a common electrolyte material for ESC. However, instead of the thin ceramic electrolyte substrate a sintered 3YSZ (Z-101, DOCERAM) was chosen as ceramic counterpart in the joining experiments. A tape casted 3YSZ was used only for special samples made for investigations on aging in dual atmospheres.

Brazing pastes were formulated by mixing the inorganic powders (silver (Heraeus), copper oxide, and titanium hydride (both Sigma Aldrich)) in appropriate ratios. Two braze compositions were employed in this study: Ag-4CuO containing 96 mol-% Ag and 4 mol-% CuO and Ag-4CuO-0.5TiH₂ with 4 mol-% CuO and 0.5 mol-% TiH₂ in silver. A cellulose based screen printing binder was added to receive brazing pastes with a solid content of 82 mass-%. The brazing pastes were screen printed on the Crofer and dried in an oven. After drying the braze thickness was approx. 120 µm.

The brazing process was done in a muffle furnace with a heating and cooling rate of 5 K/min and a brazing temperature of 1000°C. The brazing time was 20 min. In order to estimate the durability and reliability of silver based RAB brazes at 850 °C brazed gas tightness samples were annealed in air for 200, 500, and 800 h in a similar muffle furnace. Additionally, some special designed gas tightness samples were aged in dual atmospheres at 850 °C to simulate SOFC conditions. More details on the special test rig used for aging in dual atmospheres can be found in [6].

Before and after aging the gas tightness of the reactive air brazed samples was measured using a helium leak detector (Phoenix XL30, Oerlikon Leybold Vacuum, Cologne, Germany). In case of SOFC, samples with a normalized leak rate of $1 \cdot 10^{-8}$ mbar·l/(s·cm) or better will be rated as gastight. Microstructural analysis of the joints was performed on polished cross-sectioned samples using a scanning electron microscope (NVision 40, Carl Zeiss SMT, Oberkochen, Germany). The micrographs shown in this paper were recorded in the element specific back scattered electron mode. Additionally, the scanning electron microscope is equipped with an energy dispersive X-ray analysis system (abbrev. EDX / Inca x-sight, Oxford Instruments, Abingdon, England), which allows a quantitative detection of elements.

3. Results

Microstructure before aging

Figure 1 shows the micrograph of cross section of Crofer/3YSZ joints with Ag-4CuO. After brazing, an interfacial layer with a mean thickness of 3-6 µm was formed on the braze-metal interface. The reaction layer, which is shown in more detail in Figure 2(a), consists of two phases: a thin oxide scale directly on the steel surface and a thicker oxide phase. EDX analysis reveals a mixed oxide, containing mainly chromium and copper (marked Cu-Cr-O in Figure 2), which is in good agreement with the literature [15]. Occasionally, an iron-rich mixed oxide (Cu-Fe-Cr-O) can be found. The thin oxide scale between the surface of the Crofer and the copper-chromium mixed oxide consists of chromium and oxygen (Cr-O) and was identified as Cr₂O₃. Additionally, the micrographs show the formation of small pores on the steel surface underneath the oxide scale. In contrast, at the interface between the surface of the 3YSZ and the braze no closed reaction layer is formed and only small fractions of Cu-Cr-O particles are found.

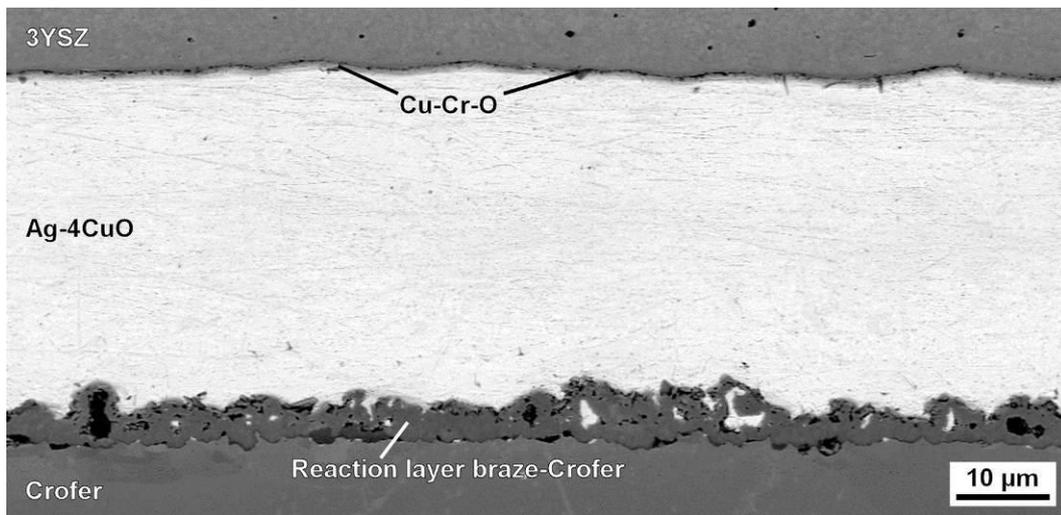


Figure 1: Microstructure of Crofer/3YSZ joints brazed with Ag-4CuO.

The microstructure of Crofer/3YSZ joints brazed with Ag-4CuO-0.5TiH₂ show only small differences in comparison to joints with Ag-4CuO. As shown in Figure 2(b) the interfacial reaction layer between braze and Crofer exhibits a similar morphology and the same mixed oxide phases as with Ag-4CuO. However, at certain sites at the reaction layer towards the Crofer an oxide phase containing copper and titanium is visible (Cu-Ti-O). In contrast to the interface between Ag-4CuO and 3YSZ, in the Crofer/3YSZ joints brazed with Ag-4CuO-0.5TiH₂ copper oxide particles incorporating titanium were found at the interface braze-3YSZ.

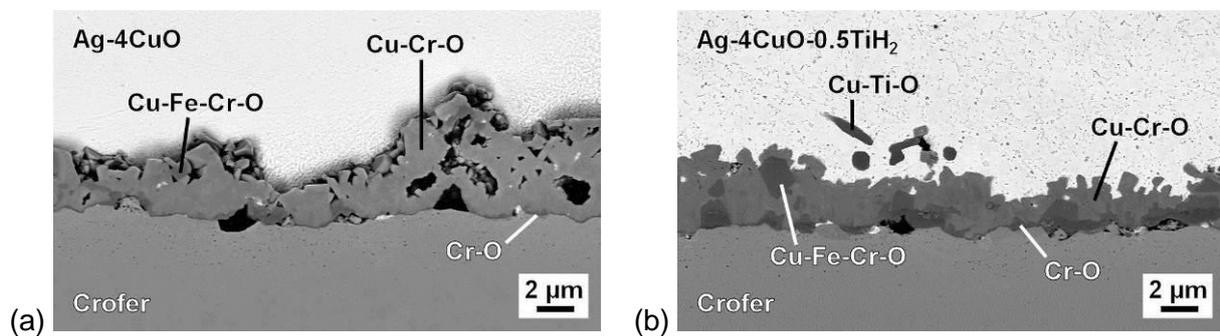


Figure 2: Comparison of interfacial reaction layers between braze and Crofer of Crofer/3YSZ joints brazed with (a) Ag-4CuO and (b) Ag-4CuO-0.5TiH₂.

Gas tightness before and after aging

The gas tightness of brazed joints is one of the major parameters for evaluation of brazing processes, due to the fact, that sealing materials for SOFC and the manufactured seals has to maintain their gas tightness all-time during SOFC operation. The helium leak rates for different Crofer/3YSZ joints before and after aging are shown in Figure 3. After furnace brazing samples made with Ag-4CuO are gastight with $7 \cdot 10^{-10}$ mbar·l/(s·cm), whereas samples made with Ag-4CuO-0.5TiH₂ have a leak rate of $5 \cdot 10^{-11}$ mbar·l/(s·cm). However, after aging for 800 h at 850°C in air no major changes of the leak rate was observed. All tested samples (three samples for each composition) maintained their gas tightness. In contrast, the aging for 800 h at 850°C in dual atmospheres causes a dramatic change in leak rate. Crofer/3YSZ joints brazed with Ag-4CuO were strongly damaged after aging, thus no leak rate value can be determined by helium leak measurement. Samples brazed with Ag-4CuO-0.5TiH₂ have lost their gas tightness as well, and the helium leak rate was grown to $7 \cdot 10^{-4}$ mbar·l/(s·cm).

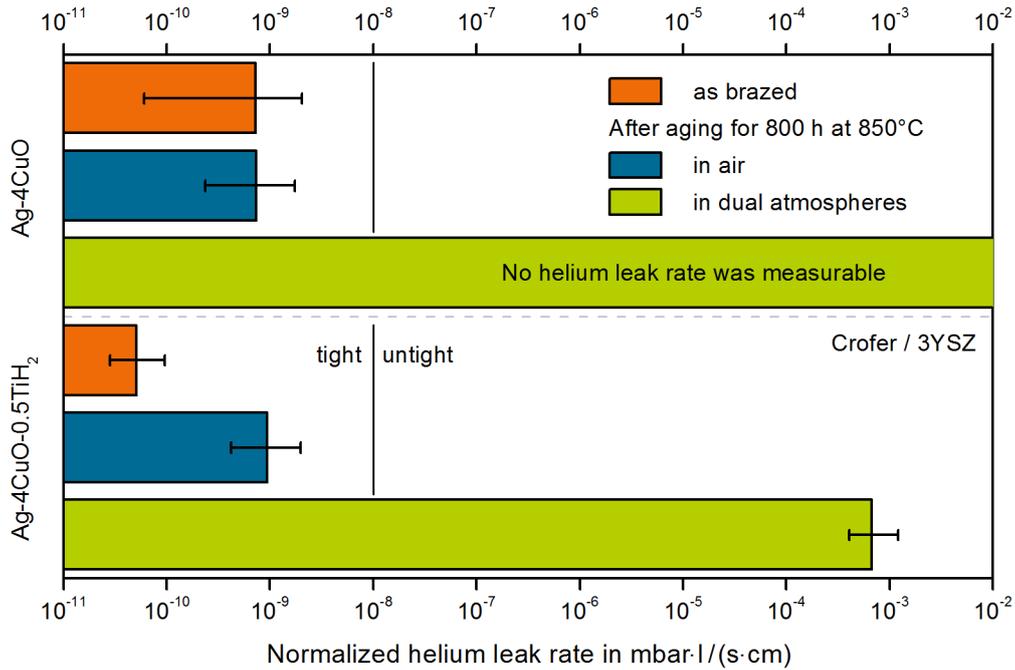


Figure 3: Gas tightness of reactive air brazed samples before and after aging in air and in dual atmospheres.

Microstructure after aging in air

The microstructure of Crofer/3YSZ joints brazed with Ag-4CuO after aging in air is shown in Figure 4. During aging for 800 h at 850 °C the microstructure at the interface between braze and Crofer is altered strongly as the interfacial layer was grown and the thickness increased to 8 μm. In contrast, the interface between braze and 3YSZ remained nearly unchanged.

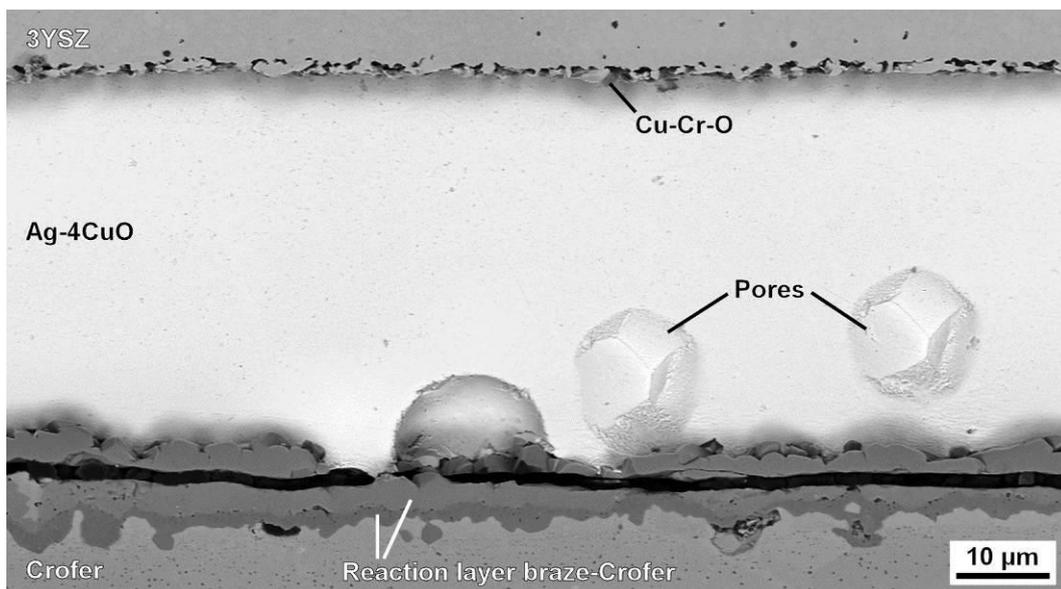


Figure 4: Microstructure of Crofer/3YSZ joint brazed with Ag-4CuO after aging for 800 h at 850°C in air. Please note: The crack is an artifact from sample preparation.

A more detailed view of the microstructure of Crofer/3YSZ joints brazed with Ag-4CuO and Ag-4CuO-0.5TiH₂ after 800 h aging time is shown in Figure 5. The changes in microstructure during aging in air and the general growth of the interfacial oxide scale indicate that the copper-chromium oxide phase formed during brazing is not stable at 850°C in air. After aging, the main phase of the interfacial layer consists of a mixed oxide containing chromium, copper and manganese (Cr-Cu-Mn-O) with small traces of titanium for joints with Ag-4CuO-0.5TiH₂. Towards the Crofer a continuous chromium oxide scale (Cr-O) with a thickness of 1-2 μm, a new mixed oxide phase consisting of chromium and manganese, and the formation of pores was found. After all, the driving force for the further oxidation of brazed joints are the diffusion of chromium and manganese from the Crofer. Additionally, inside the Crofer the precipitation of titanium oxide is visible. This phenomenon was already observed in oxidation studies of Crofer [18]. In the case of Ag-4CuO-0.5TiH₂, the formation of silver islands underneath the interfacial layer was detected, Figure 5(b).

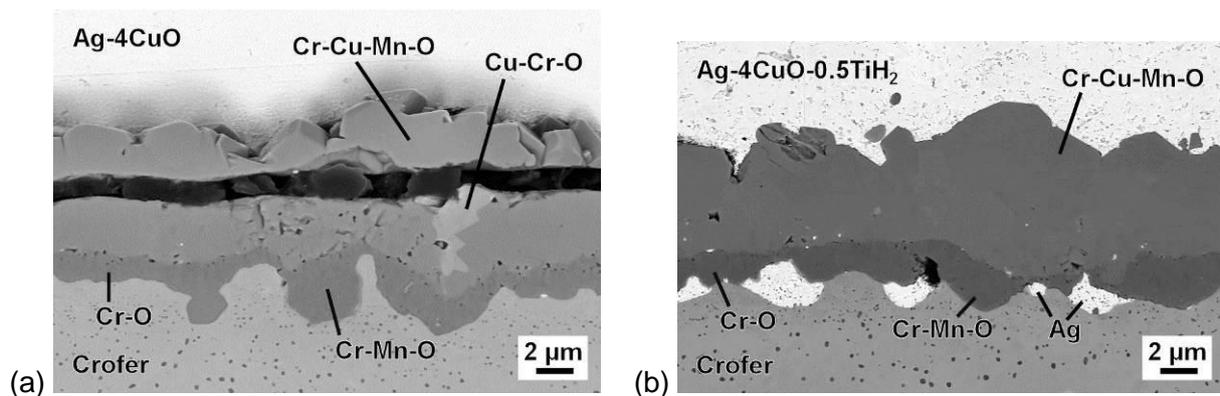


Figure 5: Comparison of interfacial reaction layers between braze and Crofer of Crofer/3YSZ joints brazed with (a) Ag-4CuO and (b) Ag-4CuO-0.5TiH₂ after aging for 800 h at 850°C in air.

For a final evaluation of the observed microstructural changes the mechanical properties of the ceramic-metal joints should be discussed. As described in more detail in [19] and [20], the phase transformation of the interfacial layer between braze and Crofer during aging in air, the increase in thickness and volume, and the formation of pores in the oxide layers resulted in an embrittlement of the aged Crofer/3YSZ joints and in a reduction of the 4-point bending strength. Additionally, it is shown that the braze composition have neither a significant effect on the formation and growth of the interfacial layers nor on the residual 4-point bending strength after aging of reactive air brazed ceramic-metal joints [20].

Microstructure after aging in dual atmospheres

In contrast to the aging in air, the aging in dual atmospheres at 850°C leads to more severe effects, thus the samples lost their gas tightness after 800 h aging time. Figure 6 shows an overview on the microstructure of a Crofer/3YSZ joint brazed with Ag-4CuO after aging in dual atmospheres. The loss of the gas tightness might be attributed to the formation of pores in the brazing seam and to the destruction of the 3YSZ. More detailed micrographs of the air and the fuel side of the aged samples are shown in Figure 7. The microstructure at the air side in Figure 7(a) shows no differences to the microstructure after aging in air (compare with Figure 5(a)). The oxidizing environment on this side of the joint caused the growth of the interfacial layer between braze and Crofer with similar phase compositions as observed during aging in air. Additionally, Figure 7(c) shows another site along the air side of the joint where instead of a chromium-rich copper oxide (Cr-Cu-Mn-O) an iron-rich copper oxide phase (Fe-Cu-Cr-O) with a thickness up to 18 μm was formed. At

the interface between the 3YSZ and the braze the well-known copper-chromium oxide particles were found if a chromium-rich copper oxide is found at the interface between the Crofer and the braze. In the case, that iron-rich copper oxides were formed at the braze-Crofer interface, the copper-chromium oxide particles at the braze-3YSZ interface were enriched with iron [20].

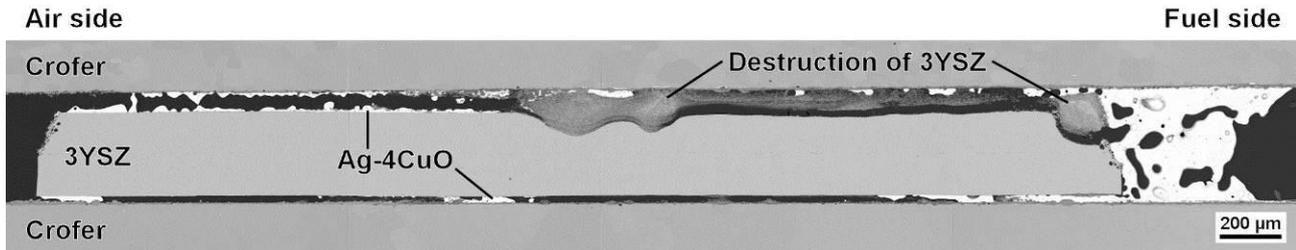


Figure 6: Microstructure of Crofer/3YSZ joint brazed with Ag-4CuO after aging for 800 h at 850°C in dual atmospheres.

The microstructure of the interfaces at the fuel side is different. The interfacial layers consist of oxides without any copper or copper oxide. The depletion of copper can be explained by the reduction of the copper oxide to metallic copper through diffusion of hydrogen into the braze [15, 16]. The reduction reaction of copper oxide with hydrogen forms water vapour, which might be responsible for formation of additional pores. The formed metallic copper is dissolved in silver. These copper-free mixed oxide phases exhibit a significant iron content, thus these phases are indicated as Cr-Fe-Mn-O and Fe-Cr-Mn-O in Figure 7(b) and (d). An increased iron content due to enhanced diffusion of iron from Crofer was also reported in [21] while aging Crofer in dual atmospheres.

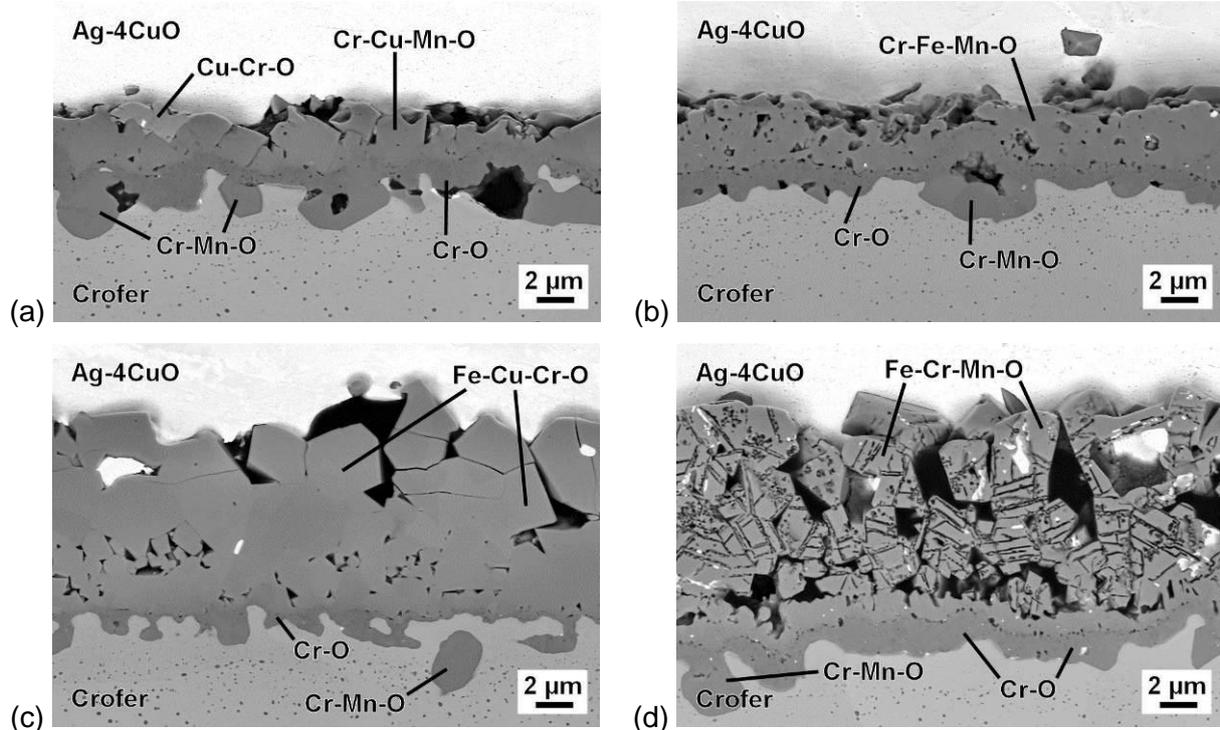


Figure 7: Comparison of interfacial reaction layers between braze and Crofer at different sides of Crofer/3YSZ joints brazed with Ag-4CuO after aging for 800 h at 850°C in dual atmospheres. (a) and (c): air side, (b) and (d): fuel side.

The depletion of copper is found along the interface braze-3YSZ as well. No copper or chromium oxide particles are found there. Moreover the iron oxide particles were detected opposite of iron-chromium mixed oxide phases. Even the destruction of the 3YSZ has been observed. Figure 8 shows single grains of 3YSZ without any interconnection and the inclusion of iron oxide along the newly formed interface. The interaction of the hydrogen containing atmosphere at the fuel side in the presence of iron oxide might cause the destruction of the 3YSZ. The solution of iron oxide in the 3YSZ which causes mechanical stresses is already known from the literature [22]. Another option that should be taken into account is the solution and dissolution of iron oxide along the grain boundary phase of the 3YSZ.

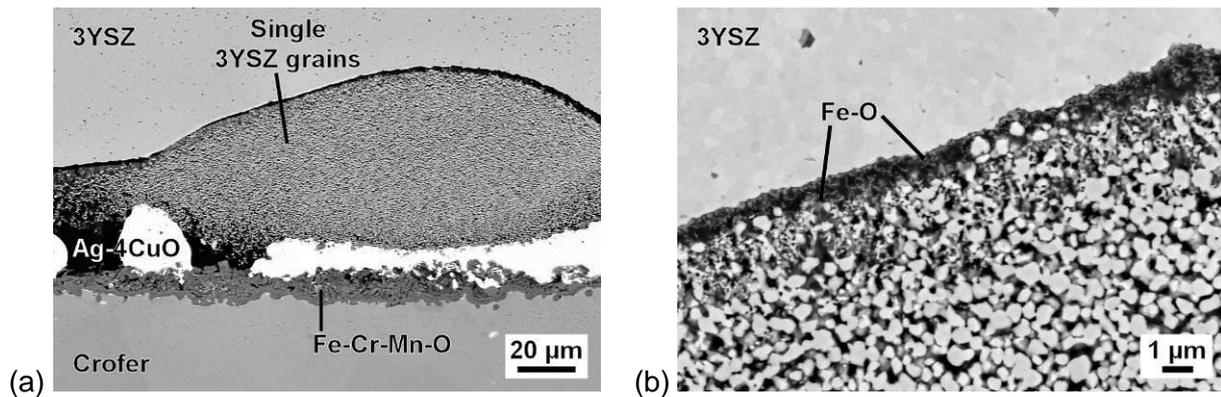


Figure 8: Corrosion of 3YSZ at the fuel side of Crofer/3YSZ joints brazed with Ag-4CuO after aging for 800 h at 850°C in dual atmospheres.

The microstructure of Crofer/3YSZ brazed with Ag-4CuO-0.5TiH₂ after aging for 800 h at 850°C in dual atmospheres is shown in Figure 9. The overview shows a much more intact brazing seam with less pore formation resulting in a better helium leak rate of these samples compared to the ones brazed with Ag-4CuO. The more detailed analysis showed only one site with beginning 3YSZ corrosion [20].

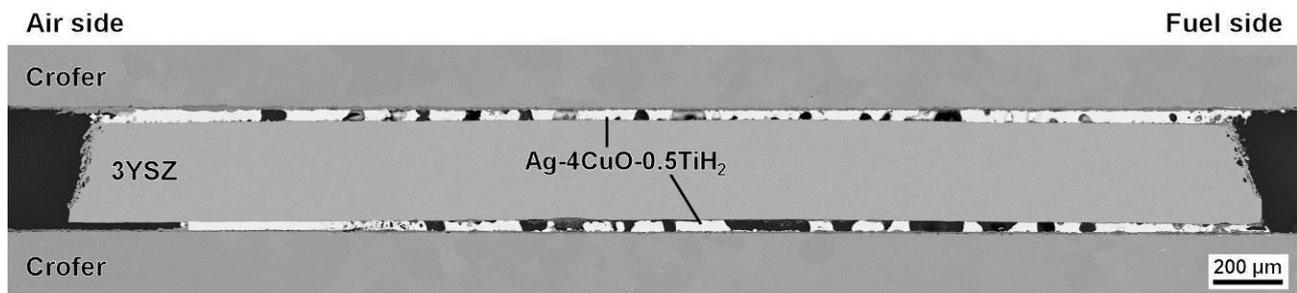


Figure 9: Microstructure of Crofer/3YSZ joint brazed with Ag-4CuO-0.5TiH₂ after aging for 800 h at 850°C in dual atmospheres.

4. Conclusion

The aging behavior of reactive air brazed seals for SOFC was examined in air and in dual atmospheres at 850°C for 800 h. All tested braze compositions led to initial helium leak rates below $1 \cdot 10^{-8}$ mbar·l/(s·cm), which means satisfactory gas tightness. Microstructural analysis of cross-sections revealed for all brazes the development of a continuous copper-chromium oxide layer with small amounts of manganese at the braze-Crofer interface and of small copper oxide particles at the braze-3YSZ interface. During aging in air at 850°C the thickness of the interfacial oxide layers grows due to diffusion of oxygen through the

silver braze and of chromium and manganese, originating from the Crofer metallic matrix. These microstructural changes has only minor effect on the gas tightness, but cause a decrease of the 4-point bending strength of reactive air brazed Crofer/3YSZ joints. Indeed, the aging in dual atmospheres causes dramatic microstructural changes in combination with a loss of gas tightness. When using Ag-4CuO a corrosive attack and destruction of the 3YSZ at the fuel side were observed and reported for the first time. It was found that the addition of small amounts of TiH₂ to the braze composition enhances the dual atmosphere tolerance of the reactive air brazed seals.

Acknowledgments

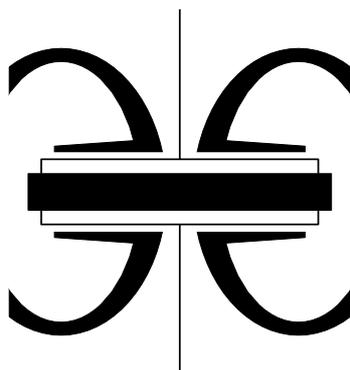
The authors thank Sébastien Arnold, Christina Frey, and Maria Striegler for sample preparation and FESEM work. This work was supported by the European Union and Free State of Saxony under contract no. 13351/2270.

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Proceedings of



11th European SOFC & SOE Forum 2014

Chapter 08 - Session A14

Interconnect, sealing and coating

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ISBN 978-3-905592-16-0

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